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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

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Sheet 2 of the certificate
Page 2 de l'attestation

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- 1 -

"A phase change ink composition"

The invention relates to a ceramic ink composition and to a method of production. The invention relates particularly to an ink composition for ink jet printing.

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The development of inkjet printing over the past few decades has seen the technology develop from purely office printer applications into a diverse range of new applications. Inkjet technology is currently employed on an industrial scale to print onto various substrates including plastics, metals, ceramics, textiles and of course paper. As the technology has become more refined the speed and versatility has improved allowing it to be used in very high speed applications such as marking and labelling.

The inkjet process allows efficient colour printing, which is unparalleled by any other printing process. Inkjet printers produce a wide variety of colours by printing four basic colours i.e. cyan, magenta, yellow and black. In conventional inkjet printers the inks used are generally based on a solvent carrier material, which contains an organic dye. Depending on the properties of the substrates other ink systems, including phase change, or hot melt, and ultraviolet curable, have been developed which give different drying characteristics. The organic dyes used can fade in colour over a period of time particularly if they are exposed to light and/or heat. Therefore, recent years have seen a growing interest in the development of more stable pigmented inks.

Ceramic inks have been provided, for example, as described in United States Patent Specification No. US4390565 and US5212212. These inks are based on a UV cureable ink system and were designed to be applied by a screen printing process. Therefore, the inks do not possess the required properties to allow them to be inkjet printed.

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Also as the ink is in liquid form, the powder constituents of the inks tend to sediment as a function of time in storage. This means that the inks must be constantly mixed while not in use. This also applies to other types of liquid inks e.g. solvent based inks.

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An objective of the invention is to provide an ink composition that does not possess these characteristics and that can be printed by a conventional inkjet printing process using commercially available inkjet printheads. The ink phase change, or hot melt, ink which remains as a solid while in storage and when the printer is switched off.

10 When the printer switches on the ink is heated and so that it melts to form a liquid ink. This means that no sedimentation of the ceramic particles can occur while the ink is in storage, effectively greatly increasing the shelf life of the inks.

The advantages of using an inkjet printing method over a screen printing method
15 include: 1). Images and patterns are produced and stored digitally, and therefore there is no requirement for storage of a large number of printing screens; 2) it is equally feasible to print images in small numbers or large numbers; 3) the printer can change from one image to another without shutting down; 4) each image printed can be different from the previous one; 5) edge to edge printing is possible; 6) any size of
20 image is possible; 7) process colours are possible; 8) it is possible to print onto uneven surfaces; 9) it is possible to print onto three dimensional shapes e.g. table ware; 10) and it offers greater flexibility in terms of the types of images that can be printed as well as the types of substrates that can be printed onto.

25 According to the invention, there is provided a phase change ink composition comprising a carrier material and a pigment material dispersed throughout the carrier material.

In one embodiment, the pigment material is a ceramic powder pigment.

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- 3 -

In another embodiment, the pigment material is a combination of a vitreous material, such as glass frit, and a ceramic pigment powder.

In one embodiment, the pigment material is a complex of salts of transition elements.

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In another embodiment, no pigment powder particles have a size greater than 10 μm .

In a further embodiment, the carrier has a melting point in the range of 50°C to 150°C.

10

Preferably, the carrier comprises a wax material.

According to another aspect, the invention provides a method of producing an ink comprising the steps of providing a carrier and dispersing a pigment in the carrier.

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In one embodiment, the powder dispersion in the carrier is stabilised by the addition of a dispersant to the ink composition.

In another embodiment, the powder particles are coated with dispersant molecules and are chemisorbed to the surface of the particles.

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In a further embodiment, ceramic particles are mixed with a dispersant in the presence of a solvent such as toluene.

25 In one embodiment, the dispersant coated powder is combined with the carrier by heating, wherein the temperature is sufficient to melt the carrier and to remove residual solvent, and mixing and subsequently allowing the mixture to cool so that the ink solidifies.

- 4 -

The invention will be more clearly understood from the following description of some embodiments thereof, given by way of example only with reference to Fig. 1, which is a plot indicating dispersant adsorption.

- 5 The invention provides a number of ink formulations that can be inkjet printed onto ceramic, glass, metal and other temperature resistant surfaces. The print can be subsequently fired to remove the organic constituents of the ink and to fuse the pigment constituents to the substrate. The ink consists of an organic carrier material, which has a melting point in the range of 50-150°C but preferably within the range of
- 10 100-130°C, and a powder ceramic (or inorganic) material dispersed throughout the carrier material. Preferably the carrier material is a wax material such as Parafint C77®, produced by Schuman Sasol GmbH, Hamburg, Germany, or other suitable low melting temperature organic material.
- 15 Preferably the ceramic powder is a mixture of one or more ceramic pigment materials with a suitable glass material. Preferably the glass material is a lead-borosilicate glass material. However, it may be another suitable glass material.

Alternatively the ceramic material may consist, solely, of an inorganic, or ceramic, pigment material. Alternatively, the ceramic material may be a powdered pigmented vitreous material. Alternatively, a soluble complex of salts of transition elements, which, on firing, will convert to a ceramic pigmented material may be used instead of a ceramic powder. The pigment materials may be of any colour, but is preferably black, cyan, magenta, yellow, or white or variations of these.

- 25 The ceramic material is in the form of a very fine powder with no particles greater than 10µm in size, and preferably with no particles greater than 3µm in size. The powdered materials with the correct particle size distribution may be produced by milling, sol-gel, or other powder production method. The powder particles are
- 30 maintained in dispersion in the ink and prevented from agglomeration and

- 5 -

sedimentation by the addition of a suitable dispersion stabilisation agent (dispersant) to the ink formulation.

5 The dispersion of the ceramic powder in the carrier material is produced by first mixing the powder with a suitable solvent. Preferably the solvent is toluene. The proportions of powder and solvent are approximately 5g powder per 100ml toluene. A suitable dispersion stabilising agent (dispersant) is added to the mixture. The proportion of dispersant added is in the range of 0 – 20% of the weight of the ceramic powder. However, preferably the proportion of dispersant added is 3.5 to 4.5% of
10 the weight of the ceramic powder. Preferably the dispersant will be 12-hydroxyoctadecanoic acid, however it may alternatively be stearic acid, or other suitable dispersant.

The mixture is then combined thoroughly by ball milling for 24 hours which breaks
15 up agglomerates and coats the particles with the dispersant. After mixing, the toluene is removed by filtration, evaporation, or other suitable means. The powder is thus coated with dispersant, however, at this point in the process the dispersant is relatively weakly bonded (physisorbed) to the surface of the particles. The dispersant coated powder is then dried in an oven for up to 24 hours at a temperature of 130°C
20 in order to remove any remaining toluene and to form a stronger bond (chemisorbed) between the dispersant molecules and the surface of the powder particles. The powder is then ready to be dispersed in the carrier material.

Other additives to the ink composition may include binders, plasticisers, dyes,
25 biocides, antioxidants or other as appropriate.

The powder composition is mixed with the carrier material in a heated vessel with accurate temperature control. The mixture is heated in order to melt the carrier material and to remove any residual solvent. The molten carrier material and the
30 dispersant coated powder are mixed by stirring or other suitable mixing technique.

- 6 -

The mixture may be maintained inside a partial vacuum during mixing in order to minimise the amount of dissolved air in the ink. After mixing, the mixture is allowed to cool so that it solidifies. The solidified material is then the ink.

- 5 The ink properties are appropriate for printing by a suitable piezo-drop-on-demand inkjet printer. The viscosity is in the range 20 to 35cP, and preferably 20 to 30cP. However, other suitable printing techniques may be employed as appropriate. The printing process or printer may include the following features: an ink reservoir with suitable heating capability which can be employed to melt the ink as required.
- 10 An ink umbilical which may be heated in order to transport the ink from the reservoir without allowing the ink to solidify during the printing process, or a piezo-drop-on-demand inkjet printhead with inbuilt heating capability which can maintain the ink in the liquid form during printing. Also the heating capability of the printhead may control the temperature of the ink so as to optimise the viscosity of
- 15 the ink.

The ink may be printed onto a variety of substrates including glass, ceramic and metal substrates. After printing the printed ink and substrate may be fired, preferably at a temperature between 740°C and 750°C, in order to remove the carrier material

20 and other organic ingredients and to fuse the ceramic material, from the ink, to the substrate. Examples of industrial applications for the invention may include decorating ceramic tiles, decorating glass articles, decorating ceramic and glass tableware, temperature resistant marking and labelling, and decorating metal articles.

- 25 In more detail, the following is an example of production of an ink.

The desired particle size distribution of the ceramic powder was produced by attrition milling. The milling involved placing a quantity of the powder in a ceramic vessel with a quantity ceramic beads. To this water was added and the contents were

30 stirred at high speed with a ceramic stirrer. At different time intervals samples of the

- 7 -

powder/water mixture were extracted and the particle size distribution was determined by a laser diffraction particle size analysis technique. The results of the particle size analysis of samples of powder after various attrition milling times are presented in Table 1.

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Milling time	Max. particle size (µm)	Min. particle size (µm)
Before milling	50	0.2
1 Hour	45	0.2
3.5 Hours	20	0.15
5 Hours	2.5	0.15

Table 1. Particle sizes of powder samples after attrition milling for 1, 3.5, and 5 hours.

10 The results of the particle size analysis was confirmed by scanning electron microscopy.

15 The dispersant used was 12-hydroxyoctadecanoic acid which is a solid material at room temperature. In order to optimise the amount of dispersant required to coat the ceramic particles an extra process step was developed. The process involved combining the dispersant and ceramic powder in various proportions in a 100ml container.

20 3g of ceramic powder was placed in a container. 50g of ceramic pellets and 65ml of toluene solvent were then added to the powder mixture and the container was sealed. The contents were ball milled for 24 hours. The solvent was removed by filtration. The coated powder was then washed with toluene to remove any non-adsorbed dispersant and was dried in an oven at 130°C for 24 hours.

25 The wax material used wax Paraflint C77[®] supplied by Schuman Sasol GmbH, Hamburg, Germany. The dispersant coated powder was then combined with the

- 8 -

solid wax in a beaker. 20 ml of toluene then added to wet the powder. The mixture was heated to 80°C to melt the wax. The resultant liquid mixture was then stirred and the temperature was raised to 110°C to evaporate the toluene. Stirring was continued for 16 hours. The ink is then cooled and solidified. Experimental phase change ink formulations are presented in Table 2.

Sample	Wax	Ceramic Powder	Dispersant
Material	Paraflint C77	White pigmented	12-hydroxyoctadecanoic acid
P1001	70	30	0
P1002	69.55	30	0.45
P1003	69.4	30	0.6
P1004	69.25	30	0.75
P1005	68.1	30	0.9
P1006	68.95	30	1.05

Table 2. Phase change ink formulations expressed in wt%.

Adsorption test

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To gain more information on the optimum amount of dispersant an adsorption test was developed which involved varying the amount of dispersant added to the powder and combining the dispersant and powder as described above. Samples of the dispersant coated powders were analysed by thermogravimetric analysis to determine the amount of adsorbed dispersant in each sample. Thermogravimetric analysis involves controlled heating of a small amount of the sample in a highly sensitive balance. As material is burned off, the balance detects a weight loss and the temperature at which it occurs. The aim was to achieve the maximum weight loss as this will represent the maximum amount of adsorbed dispersant. Also it is desirable to maximise the temperature at which the dispersant burns off as a higher

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- 9 -

temperature represents stronger adsorption of the dispersant to the powder. The adsorption test sample compositions are presented in Table 3 below. The ceramic powder and dispersant contents are expressed in terms of weight percent of the total solids content.

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Sample	Toluene (ml)	Powder Wt%	Dispersant Wt %
A001	65	100	0
A002	65	99	1
A003	65	98	2
A004	65	97	3
A005	65	96	4
A006	65	95	5
A007	65	94	6
A008	65	93	7
A009	65	90	10
A010	65	88	12
A012	65	86	14
A013	65	80	20

Table 3. Powder-dispersant-mixtures.

The results of the thermogravimetric analysis are presented in Table 4.

Sample	Weight Loss (%)	% Dispersant adsorbed
A001	0	0
A002	0.38	36
A003	1.62	81
A004	2.79	93
A005	3.04	76
A006	3.51	70.2

- 10 -

A007	4.19	69.83
A008	4.7	67.14
A009	5.77	57.7
A010	7.32	61
A012	9.46	67.57
A013	11.83	59.15

Table 4. Results of adsorption test thermogravimetric analysis.

By plotting the weight loss results as a percentage of the weight of the dispersant added, as in Figure 1, it can be seen that the amount of adsorbed dispersant increases rapidly up to approximately 2.8% weight loss which corresponds to a powder to dispersant ratio of 97:3 by weight. This is the minimum amount of dispersant that was then used in the production of wax based inks.

Viscosity.

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Viscosity of the inks was determined by cone and plate rotational viscometry employing a Haake RV-1 rotational viscometer with temperature control attachments.

15 The test involves placing the sample between a cone and a plate of standard geometry. The cone is rotated at a preset speed. The torque required to maintain the rotational speed is related to the viscosity. The viscosity is calculated from the torque required, the set speed and the geometry factors, shear force and shear rate are also calculated.

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The viscosity and shear force were determined for each sample at varying shear rate.

Dispersion stability

- 11 -

25ml samples of each phase change ink were placed in 25ml graduated cylinders. Stoppers were placed on the cylinders to avoid evaporation. The cylinders were placed in an oven at 110°C.

- 5 The cylinders were then allowed to stand at 110°C for 72 hours. The sedimentation volume was recorded at times of 1, 2, 4, 8, 12, 24, 48 and 72 hours.

The invention is not limited to the embodiments described but may be varied in construction and detail.

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- 12 -

Claims

1. A phase change ink composition comprising a carrier material and a pigment material dispersed throughout the carrier material.
- 5 2. A phase change ink composition as claimed in claim 1, wherein the pigment material is a ceramic powder pigment.
- 10 3. A phase change ink composition as claimed in claim 1, wherein the pigment material is a combination of a vitreous material, such as glass frit, and a ceramic pigment powder.
- 15 4. A phase change ink composition as claimed in claim 1, wherein the pigment material is a complex of salts of transition elements.
5. A phase change ink composition as claimed in any preceding claim, wherein no pigment powder particles have a size greater than 10 μm .
- 20 6. A phase change ink composition as claimed in any preceding claim, wherein the carrier has a melting point in the range of 50°C to 150°C.
7. A phase change ink composition as claimed in an preceding claim, wherein the carrier comprises a wax material.
- 25 8. A method of producing an ink comprising the steps of providing a carrier and dispersing a pigment in the carrier.
9. A method as claimed in claim 8, wherein the powder dispersion in the carrier is stabilised by the addition of a dispersant to the ink composition.

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- 13 -

10. A method as claimed in claims 8 or 9, wherein the powder particles are coated with dispersant molecules and are chemisorbed to the surface of the particles.
- 5 11. A method as claimed in claims 8, 9, or 10, wherein ceramic particles are mixed with a dispersant in the presence of a solvent such as toluene.
12. A method as claimed in any of claims 8 to 11, wherein the dispersant coated powder is combined with the carrier by heating, wherein the temperature is
10 sufficient to melt the carrier and to remove residual solvent, and mixing and subsequently allowing the mixture to cool so that the ink solidifies.

- 14 -

ABSTRACT

“A phase change ink composition”

- 5 Phase change (hot melt) ink is produced for ink jet printing. The ink has a carrier and a powder ceramic dispersed throughout the carrier. The powder grain size is under $3\mu\text{m}$. For production, a dispersant and a solvent are added, the solvent being later removed leaving dispersant physisorbed to the powder. The coated powder is heated to create stronger bonds (chemisorbed) and remove any remaining solvent
- 10 (e.g. toluene).

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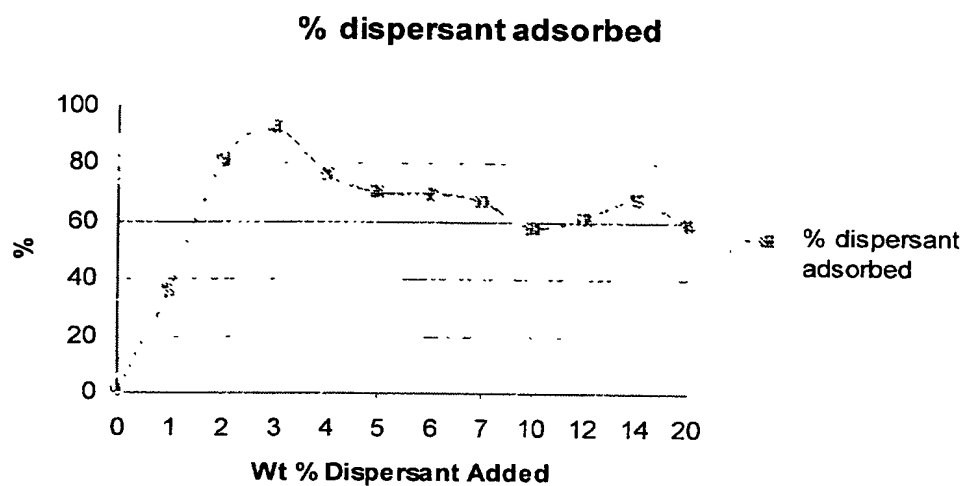


Figure 1. Percentage of dispersant adsorbed Vs. amount added.

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